

## MICROWAVE ASSISTED ACID DIGESTION OF LIQUID SAMPLES AND EXTRACTS

## 1.0 SCOPE AND APPLICATION

- 1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis, by inductively coupled plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. The method referenced with in this SOP is SW-846 Method 3015A. This SOP is for use on all samples that do not require Ohio VAP certification.
- 1.2 Samples prepared by using nitric acid digestion are analyzed by ICP-MS for the following metals:

<u>Metal (Symbol)</u>	<u>CAS#:</u>
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Boron (B)	7440-42-8
Beryllium (Be)	7440-41-7
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-95-4
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Strontium (Sr)	7440-24-6
Thallium (Th)	7440-28-0
Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

## 2.0 SUMMARY OF METHOD

- 2.1 A representative 0.5 to 25 g/ml aqueous sample is digested in 1 ml of concentrated nitric acid in a polypropylene digestion vessel brought to a final volume of 50 ml and heated using microwave heating. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle prior to analysis.

## 3.0 INTERFERENCES

- 3.1 Addition of nitric acid to samples that contain organics, such as TCLP extracts, could result in a violent reaction and splattering (loss) of the sample, leading to loss of analytes and/or sample, which must be avoided. A smaller sample size can be used but the final water volume must be adjusted to approximately 10 ml prior to the heating stage.

## 4.0 APPARATUS AND MATERIALS

## 4.1 Microwave Digestion System CEM–Model MDS – 81D and MARSX-Model # 907600

4.1.1 The MDS-81D consists of a microwave drying system with an operator selectable power output of 0-600 watts in 1% increments, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon<sup>®</sup> coated cavity, exhaust tubing and standard screen rotating turntable, rotated at 6 rpm to insure uniform microwave heating.

4.1.2 The MARSX consists of a microwave drying system with an operator selectable power output of 0-1200 watts in, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon<sup>®</sup> coated cavity, exhaust tubing and standard rotating turntable, and self calibration features.

## 4.1.3 Microwave Digestion System Specifications:

MDS-81D		MARSX	
Power	600 Watts	Power	1200 Watts
Pressure	0 - 200 psi	Pressure	0 - 200 psi
Temperature	0 - 200°C	Temperature	0 - 200°C
Capacity	26 samples	Capacity	50 samples

4.2 Analytical balances, 510g capacity, minimum accuracy  $\pm 0.001$ g and 250g capacity, minimum accuracy  $\pm 0.0001$ g.

4.3 Filter funnel, glass or disposable polypropylene.

4.4 Glass-fiber filter paper, 0.45  $\mu$ m.

4.5 Membrane filters, 0.45  $\mu$ m.

4.6 Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.

4.7 Disposable polypropylene vessels, 50 ml, compatible with centrifuge.

4.8 Plastic containers to support minimum of 200 ml.

4.9 Disposable Pasteur pipettes.

4.10 Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50  $\mu$ l to 5,000  $\mu$ l.

4.11 Centrifuge (IEC Centra GP8)

## 5.0 REAGENTS

5.1 Trace metal grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, if applicable.

5.2 Deionized (DI) Water (Type I) is used which meets the specifications of the ASTM<sup>[1]</sup> standard criteria.

5.3 Concentrated nitric acid, HNO<sub>3</sub>, Trace Metal Grade. Acid purity is monitored by analysis of the laboratory reagent blank.

5.4 Standards added to digestion:

## 5.4.1 Spiking Solutions

<sup>[1]</sup> 1985 Annual Book of ASTM Standards, Vol.11.01; “Standard Specification for Reagent Water”

- 5.4.1.1 Spiking solutions are prepared according to the Standard Prep Log. The formula, date source solutions, lot numbers, expiration date of stock standards, expiration date standard made, expiration and unique ID of any working standards used.
- 5.4.1.2 All standards are NIST traceable.
- 5.4.1.3 Multi-element standard solution WS1 (see standard prep book), containing Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mo, Mn, Ni, Se, Ag, Tl, Ti, V, Zn. This solution is made from stock NIST traceable standard and prepared according to the standard prep book.
  - 5.4.1.3.1 WS1 is used to make the QC Spiking Solution. The QC Spiking Solution is used to spike the LCS, MS, and MSD samples prior to digestion.
- 5.4.1.4 Multi-element standard solution HM (see standard prep book), containing 100 µg/ml each of Ca, K, Mg, Na. From this solution, 1.0 ml is added to the QC samples (*i.e.* MS/MSD samples), and 0.50 ml to the laboratory control sample (LCS), by weighing the amounts (1.0 g, 0.50 g) on the scale).

#### 5.4.2 Internal Standards (After digestion):

- 5.4.2.1 Lithium 6, 1000 µg/ml stock solution.
- 5.4.2.2 Scandium, 1000 µg/ml stock solution.
- 5.4.2.3 Yttrium, 1000 µg/ml stock solution.
- 5.4.2.4 Rhodium, 1000 µg/ml stock solution.
- 5.4.2.5 Rhenium, 1000 µg/ml stock solution.
- 5.4.2.6 Internal Standard working solution (IS-WS): From the above stock solutions, 2.5 g of each is transferred to a 1000 ml plastic bottle, along with 10 ml of concentrated HNO<sub>3</sub> and brought to a final volume of 1000 ml (by weight). The concentration in the flask will be 2.5 µg/ml. This represents the internal standards working solution from which 1 ml will be added to all samples (*i.e.* standards, samples, QC samples, blanks, etc.) prior to the analysis by the ICP/MS.

*NOTE: The stock solutions are NIST traceable and provided with a certificate of analyses and MSDS sheets by the manufacturer.*

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 6.1 All samples are collected in appropriate containers. The samples are collected in HNO<sub>3</sub> pre-preserved plastic container and are acidified to pH of <2. (Approximately 125 ml volume).
- 6.2 Holding times for metals are 6 months from the date of sampling, with the exception of Mercury, which is not covered by this SOP.

## 7.0 PROCEDURE

- 7.1 Calibration of Microwave Equipment
  - 7.1.1 Microwaves are calibrated once a year according to the manufactures instructions.
- 7.2 All digestion vessels are disposable and are used only once, which allows for better sample control and prevents cross contamination.

**CAUTION:** -Toxic nitrogen oxide fumes may evolve, therefore all work must be performed in a properly operating ventilation system.  
- Loss of sample through splattering inside the microwave system must be avoided. Physical observation is sufficient to determine if this is the case, therefore the batch of samples needs to be inspected at the end of the digestion cycle. If splattering has occurred, the samples are to be discarded, and a new batch is to be prepared.

### 7.3 Digestion using industrial Microwave.

- 7.3.1 A 0.5 to 25 ml/grams aliquot of a well shaken sample is transferred into the digestion vessel, sample volume is determined by sample matrix and sample history. The vessel is labeled with the sample number, which is also recorded on the preparation sheet.
- 7.3.2 With every batch of 20 analytical samples measure a volume of reagent water equal to the sample volume as described at 7.3.1 into a vessel labeled LRB. This represents the Laboratory Reagent Blank (LRB), which is carried through the entire digestion procedure, the same as an analytical sample.
- 7.3.3 With every batch of samples measure a volume of reagent water equal to the sample volume as described at 7.3.1 into a vessel labeled LCS. This represents the Laboratory Control Sample (LCS), which is carried through the entire digestion procedure, the same as an analytical sample.
- 7.3.4 For every 10 samples measure, in a similar manner, an amount equal to the parent sample of the sample designated for Matrix Spike (MS) and Matrix Spike duplicate (MSD) or duplicate (Dp).
- 7.3.4.1 Spiking for liquid samples is done by adding 0.5 ml of 5 ppm QC Spiking Solution.
- 7.3.5 Add 1 ml of concentrated nitric acid to each vessel, by using the bottle top dispenser in the hood.
- 7.3.6 For analysis of all metals except Ca, Mg, K and Na, add 0.5 ml of the QC Spiking Solution to the QC samples (LCS, MS/MSD). For Ca, Mg, K and Na, add 1.0 ml of the **HM** solution to the LCS, and 1.0 ml of the **HM** solution to the MS/MSD samples. The spike concentration and the Lot # of the stock solution used is recorded in the preparation log.

**CAUTION:** Addition of nitric acid to the non-aqueous (solvents) samples needs to be performed slowly, dropwise if possible in order to control the potential reaction. When the reaction has subsided, swirl the vessel lightly, dilute the sample to approximately 10 mL, and go to the next step.

- 7.3.7 Samples are slowly ramped in the microwave to 95±4 degrees Celsius over the course of a few minutes and maintained at this temperature for 30 minutes.
- 7.3.8 After the temperature program is completed, leave the vessels 5-10 minutes in the microwave, to cool down, and then move them into the hood. Add 1 ml of the Internal Standard working solution, using an Eppendorf automatic pipettor, and dilute to the 50 ml mark with DI Water into a calibrated digestion vessel (per lot).
- 7.3.9 If the digested sample contains particulate matter, which has the potential to clog the nebulizer, the sample needs to be centrifuged, allowed to settle, or filtered.
- 7.3.10 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this, however this can frequently be accomplished in a few hours. If it does not, centrifuge or filter the sample.
- 7.3.11 Centrifugation: Centrifugation at 4500 rpm for 3 minutes is usually sufficient to clear the supernatant.
  - 7.3.11.1 Filtering: The filtering apparatus (flask and funnel) must be thoroughly rinsed with a 10% v/v nitric acid solution and copious amounts of DI Water. Filter the sample through a 0.45 µm filter paper and transfer the liquid to a new vessel. Glass fiber

filters are acceptable for all metals except Zn and Ba, for which membrane filters are required, due to the presence of these elements in the glass fiber filters.

7.3.12 Calculate the dilution factor (DF) by the formula:

$$DF = \frac{\text{Final Volume (50)}}{\text{Sample amount}}$$

7.3.13 This dilution factor is recorded in the sample preparation log, and is to be used in the determination of the final result by the ICP/MS.

## 8.0 QUALITY CONTROL

- 8.1 For each analytical batch of 20 samples processed, one laboratory reagent blank (LRB) must be carried throughout the entire sample preparation and analytical process. The LRB will be used for determining if the samples are being contaminated during preparation or from reagents.
- 8.2 For each analytical batch of 20 samples processed, one laboratory control sample (LCS) must be carried throughout the entire sample preparation and analytical process. The LCS will be used for determining the performance of the method for that particular batch.
- 8.3 Spiked samples (MS) must be employed to determine accuracy. A spiked sample must be included with each group of 10 samples processed.
- 8.4 Duplicate (Dp) samples or Matrix Spike Duplicate (MSD) must be processed for every ten samples. A duplicate sample is a real sample brought through the whole sample preparation and analytical process.
- 8.5 For each analytical batch of 20 sample processed the laboratory must perform a dilution test. The dilution test is performed by taking 10 ml of a parent sample after digestion and adding 0.8 ml of acid and 0.8 ml of internal standard and bring to a final volume of 50 ml. The dilution test is used to identify matrix interference and is not applicable if the measured concentration is less than 100 time the MDL for each measured analyte.

## 9.0 WASTE DISPOSAL

### 9.1 Samples

- 9.1.1 All digested samples are neutralized with baking soda and diluted before being disposed of with the normal laboratory waste water.
- 9.1.2 As a "small generator" of metals, Merit laboratories has been approved for this type of disposal from the local government.

### 9.2 Acid bottles

- 9.2.1 Acid bottles are rinsed out and neutralized with baking soda before being disposed of with the normal laboratory waste.

## 10.0 DOCUMENTATION

- 10.1 All pertinent information is entered into a digestion logbook. The digestion log sheet has to contain the following information on the header/table:
  - Date.
  - Analyst initials.
  - Method reference.
  - Sample #.
  - Sample weight or volume.
  - MS/MSD/LCS spike concentration.
  - Total solids (if applicable)

- Acid Lot #
- Spike Lot #
- Dilution Factor
- Prep batch
- Final volume of sample
- Remarks
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## 11.0 METHOD PERFORMANCE

- 11.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

## 12.0 REFERENCES

- 12.1 Horlick, G., et al., Spectrochim. Acta 40B, 1555 (1985).
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- 12.3 Tan, S.H., and Horlick, G., Appl. Spectrosc. 40, 445 (1986).
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- 12.5 Holden, N.E., "Table of the Isotopes," in Lide, D.R., Ed., CRC Handbook of Chemistry and Physics, 74th Ed., CRC press, Boca Raton, FL, 1993.
- 12.6 Hinnners, T.A., Heithmar, E., Rissmann, E., and Smith, D., Winter Conference on Plasma Spectrochemistry, Abstract THP18; p. 237, San Diego, CA (1994).
- 12.7 Lichte, F.E., et al., Anal. Chem. 59, 1150 (1987).
- 12.8 Evans E.H., and Ebdon, L., J. Anal. At. Spectrom. 4, 299 (1989).
- 12.9 Beauchemin, D., et al., Spectrochim. Acta 42B, 467 (1987).
- 12.10 Houk, R.S., Anal. Chem. 58, 97A (1986).
- 12.11 Thompson, J.J., and Houk, R.S., Appl. Spectrosc. 41, 801 (1987).
- 12.12 SW-846, Method 6020 Revision 0, 1994.
- 12.13 Method 200.8, Revision 5.4, 1998.
- 12.14 SW-846, Method 6020A Revision 1, 2007
- 12.15 SW-846, Method 8000C Revision 3, 2003
- 12.16 SW-846, Method 3015

## 13.0 SAFETY

- 13.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 13.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 4 times per hour and 6 times per hour when the emergency purge button is hit.
- 13.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.
- 13.4 Specific attention be paid (but not limited) to
- 13.4.1 Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.
  - 13.4.2 Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.
  - 13.4.3 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.
  - 13.4.4 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

## 14.0 APPROVAL &amp; ISSUE:

14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

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Analyst	Date
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Andy Ball, QA/QC Officer	Date
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Maya V. Murshak, Technical Director	Date
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